

MICROHOTPLATE BASED H₂ GAS SENSORS

Frank DiMeo Jr., and Barry Chen
ATMI
Danbury, CT 06810

Abstract

The United States Department of Energy has been mandated by Congress to develop the critical technologies required for the implementation of hydrogen based energy. A common need in every technology area is the ability to detect and monitor gaseous hydrogen. Hydrogen gas sensors that can quickly and reliably detect hydrogen over a wide range of oxygen and moisture concentrations are not currently available, and must be developed in order to facilitate the transition to a hydrogen based energy economy.

This paper reports our recent progress in developing MEMS (Micro-Electro-Mechanical Systems) based H₂ gas sensors. These sensors couple novel thin films as the active layer with a MEMS structure known as a Micro-Hotplate. This coupling results in a H₂ gas sensor that has several unique advantages in terms of speed, sensitivity, stability and amenability to large scale manufacture. Our preliminary results are extremely encouraging, and suggest that this technology has substantial potential for meeting the sensing requirements of a hydrogen based energy economy.

Introduction

"Hydrogen will join electricity in the 21st Century as a primary energy carrier in the nation's sustainable energy future."(DOE 1995) This bold statement was made as part of

the 1995 Hydrogen Vision and reflects the tremendous potential of hydrogen as an energy system. The abundance and versatility of hydrogen suggests that it can provide solutions to problems encountered with current fossil fuel energy systems, such as declining domestic supplies, air pollution, global warming, and national security.

Significant research and development efforts are currently underway to make the widespread use of hydrogen technically and economically feasible. These efforts are directed toward creating the basic building blocks of a hydrogen economy: production, storage, transport and utilization. An underlying need of each of these building blocks is the ability to detect and quantify the amount of hydrogen gas present. This is not only required for health and safety reasons, but will be required as a means of monitoring hydrogen based processes. For example, if hydrogen were to be introduced as an automobile fuel additive, several sensors would be needed to detect potential hydrogen gas leaks, as well as to monitor and provide feedback to regulate the air/fuel/hydrogen mixture.

Although the safety record of the commercial hydrogen industry has been excellent, it is estimated that undetected leaks were involved in 40% of industrial hydrogen incidents that did occur. (HRI/NREL 1998) Emerging hydrogen based energy systems will require hydrogen sensors that are as ubiquitous as computer chips have become in our factories, homes, and in our cars. This means that the ability to produce large volumes of sensors at a low cost is paramount. It follows naturally that the same technology that has enabled computer chips to proliferate could be used to advantage for fabrication of hydrogen sensors: namely, solid state integrated circuit technology.

In order to support an effective hydrogen detection and monitoring system, the hydrogen sensor element must fulfill several requirements. It needs to be selective to hydrogen in variety of atmospheres (including the oxygen-rich high-humidity environments found in fuel cells). It must have a good signal to noise ratio and a large dynamic range. Speed of detection is a critical requirement to ensure rapid response to potentially hazardous leaks. Long lifetimes between calibrations are desirable in order to minimize maintenance. Low power consumption is requisite for use in portable instrumentation and personnel monitoring devices. Ultimately, these must all be achieved by a safe sensor element that is affordable to manufacture in large numbers, so that safe design principles, and not costs, are the deciding factor in the number and locations of detection points.

This paper reports on our recent progress in developing MEMS (Micro-Electro-Mechanical Systems) based H₂ gas sensors. These sensors couple novel thin films as the active layer with a MEMS structure known as a Micro-Hotplate. This coupling was expected to result in a H₂ gas sensor that has several unique advantages in terms of speed, sensitivity, stability and amenability to large scale manufacture. To date, we have demonstrated a speed of response of < 0.5 s to 1% H₂ in dry air, and the ability to detect < 200 ppm. Our preliminary manufacturing analysis suggests that these can readily and inexpensively be produced at quantities of >1 million.

Experimental

Sensor Fabrication

MEMS based hydrogen gas sensors have been produced at ATMI using a 5 step process. The realization of micro-machined suspended structures via a CMOS foundry process has been described by several laboratories, (Suehle, Cavicchi et al. 1993; Cavicchi, Suehle et al. 1995; Baltes, Paul et al. 1998) and the process used in this work is as follows. First the microhotplate device structures were designed using a commercial CAD layout software package. These designs were then sent out for fabrication through the MOSIS foundry service. The as-received chips were etched at ATMI using XeF_2 to create suspended micro-hotplate device structures. The functionalization step of this process involves applying a H_2 sensitive coating to the surface of structures. The precise nature of both the materials and deposition process for this coating are proprietary to ATMI, but for the purposes of this report can be thought of as a rare-earth based film, overcoated with a palladium based layer.(Bhandari and Baum 1999) The final fabrication step was the dicing and packaging of the chips, which was done by an external vendor. Figure 1 shows a group of packaged sensors devices, and Figure 2 is a picture of an individual packaged sensor.

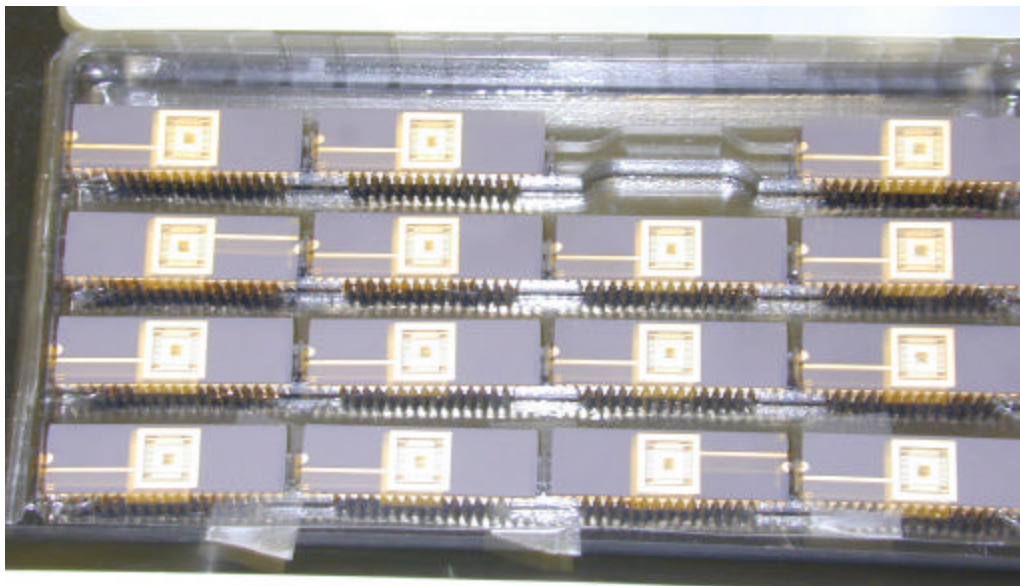


Figure 1. Optical digital photograph of several packaged microhotplate based H_2 gas sensors.

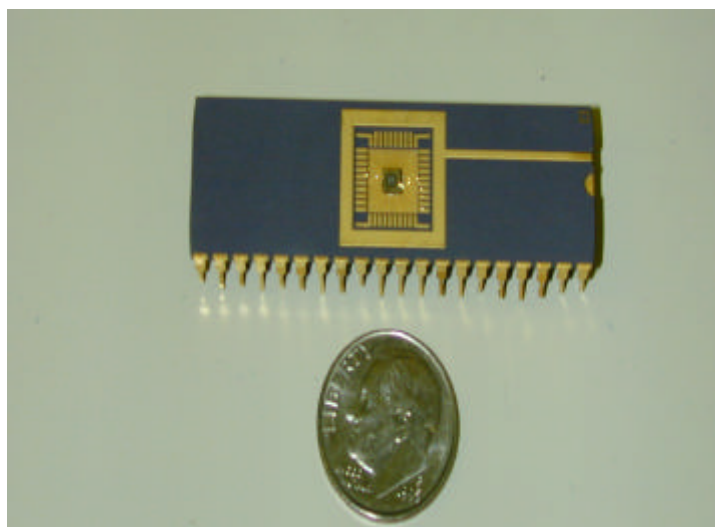


Figure 2. Optical digital photograph of an individual microhotplate based H_2 gas sensor.

H_2 Response Testing

The measured response of these gas sensors is the change in resistance that occurs in the active layer film stack when exposed to hydrogen, where the resistance of the film increases with increasing hydrogen concentration. Based on the design flexibility of the micro-hotplate, the resistance of these films can be measured in either a 2-wire or a 4-wire configuration.

Accurately measuring the speed of response to H_2 of the gas sensors was an important design consideration for both the data collection system and the gas handling manifold constructed for this program. For the data collection, we constructed an automated system based on an HP 34970A DMM data logger with an HP 34902A scanning card. This system is capable of a scanning speed of 250 channels/s. In order to achieve fast gas switching speeds, the gas handling manifold used low volume gas chromatography valves in combination with 1/8" tubing and a small test chamber size.

The ambient gas used for the experiment was triple filtered compressed air that was passed through a membrane drier, with a dewpoint specification of -40°C . Grade 5.0 hydrogen was used and blended with the air using mass flow controllers with ranges of 200 and 5000 sccm respectively.

Discussion

H_2 Gas Sensing Results

Figure 3 shows the resistive response of a micro-hotplate based H_2 gas sensor. The measurement was made in a 2-wire configuration, and the micro-hotplate was held at an

elevated temperature by passing current (< 5 mA) through the embedded polysilicon heater. In this experiment, the sensor was cyclically exposed 10 times to 0.25% H_2 in dry air. Figure 4 focuses on the transition of one particular cycle with an expanded scale. From this figure, a rise time of < 0.44 s was measured. It should also be noted that the magnitude of the response was greater than 120%. This can be compared with the typical change in response of palladium alloy resistors, which is on the order of 10% when exposed to 1 atm of H_2 . (Hunter 1996)

Figure 5 shows the response of a microhotplate to different concentrations of H_2 . In this experiment, the initial concentration was 1%, and it was decreased by a factor of 2 with each step until a final concentration of $\sim 0.01\%$ (150 ppm) was reached. The sensor was exposed two times at each concentration. The exposure time was 300 s and the time between exposures was also 300 s. The sensor exhibited detectable responses to nearly two orders of magnitude of H_2 concentration. The temperature of the hotplate was not intentionally varied in this experiment. It seems likely that the minimum detectable gas concentration can be further improved by optimizing the operation conditions at lower H_2 concentrations. Figure 6 is a plot of the responses from Figure 5 as a function of H_2 concentration. For this plot, the response was taken as the absolute change in resistance as measured from the beginning base line resistance. The H_2 concentration is plotted on a logarithmic axis, and shows that the response does not follow a simple dependence on the H_2 concentration. The reasons for the behavior of the resistivity as a function of H_2 are not currently well understood. One factor influencing the behavior of the curve in Figure 6 is the fact that at the lower H_2 concentrations, the films response does not appear to have come to equilibrium within the exposure time. In addition to this, the influence of contact resistance in a two probe configuration should be considered. Further testing is required to obtain a more accurate understanding of this behavior.

Stability is an important requirement of any type of sensor. To begin the investigation in this area, the resistance as a function of time without H_2 exposure was examined for a period of several days in dry air, as shown in the top panel of Figure 7. There was no flow over the sensor at this time. During the first day or so there is a small steady reduction in resistance, which eventually leveled out. This small drift was on the order of an ohm, which represents hydrogen in the sub-200 ppm range, and may either be due to outgassing from the sensing film, or from the chamber wall. After this, the resistance reached steady state, with a standard deviation of ~ 0.05 ohms. This resulted in a signal to noise ratio of ~ 1200 (average value/standard deviation). The middle panel of Figure 7 shows the power consumed by the polysilicon heater element of the microhotplate over the same time frame, which is expected to be representative of the operating temperature. There appeared to be cyclical variation in the power, which has a ~ 24 hour period, i.e. a day/night difference. When the resistance is multiplied by the power consumed, which, to first order, compensates for temperature, the variation appears much reduced. The signal to noise now increases to nearly 3000, and a jump in resistance on day 6, which was lost in the noise, becomes noticeable.

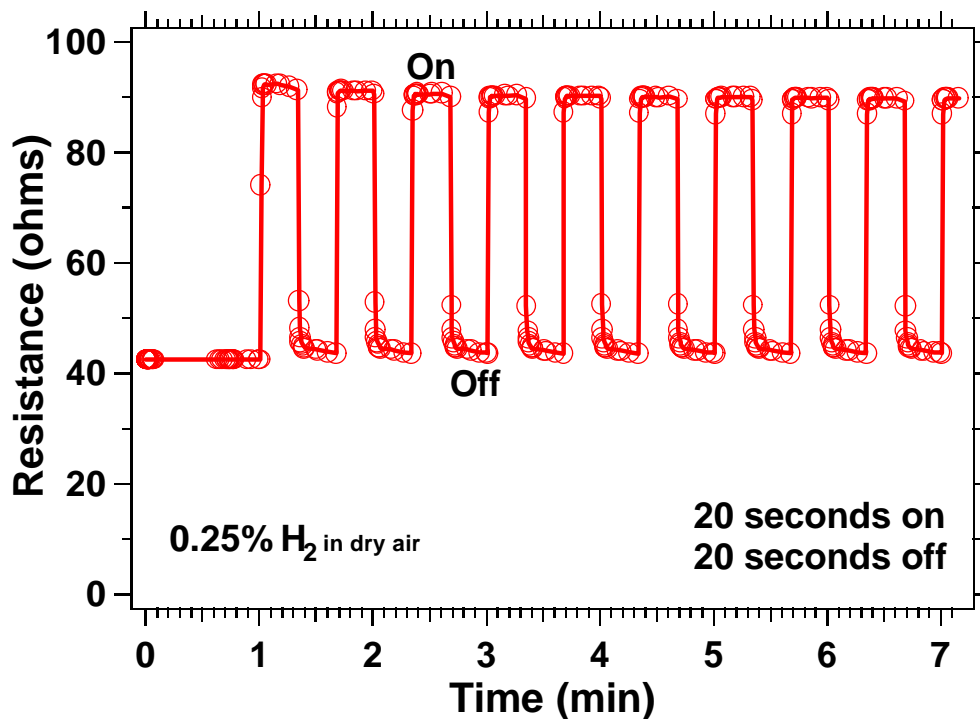


Figure 3. Resistive response of a microhotplate based H_2 gas sensor to repeated exposure to 0.25% H_2 in air. The magnitude of response is greater than 120% of the pre-exposure baseline.

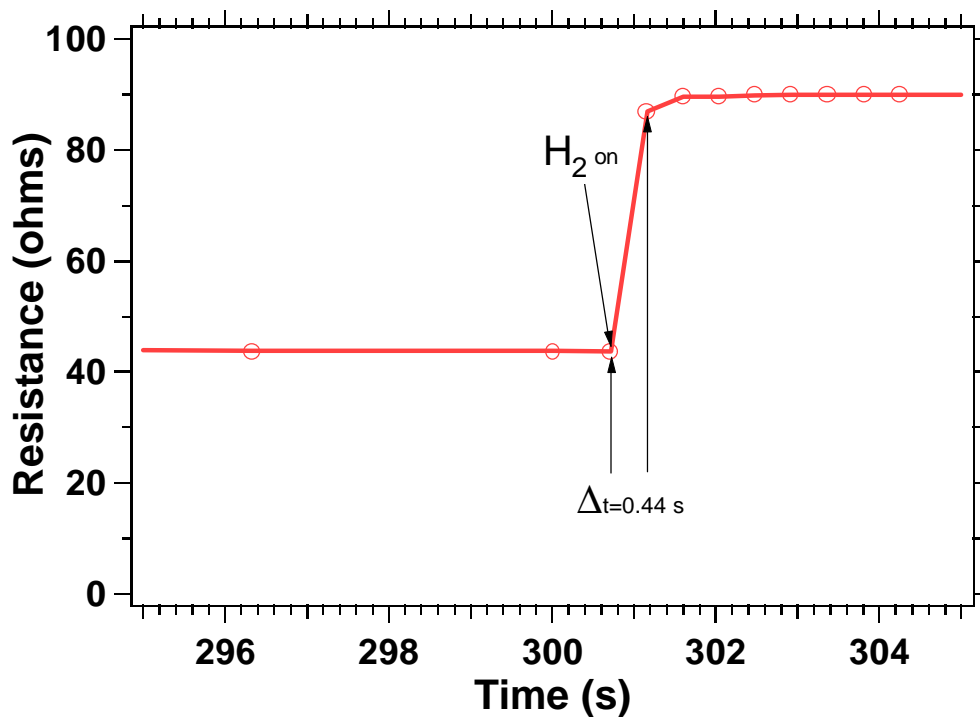


Figure 4. Expanded scale plot of the resistive response of a microhotplate based H_2 gas sensor to exposure to 0.25% H_2 in air, with a demonstrated speed of response < 0.5 sec.

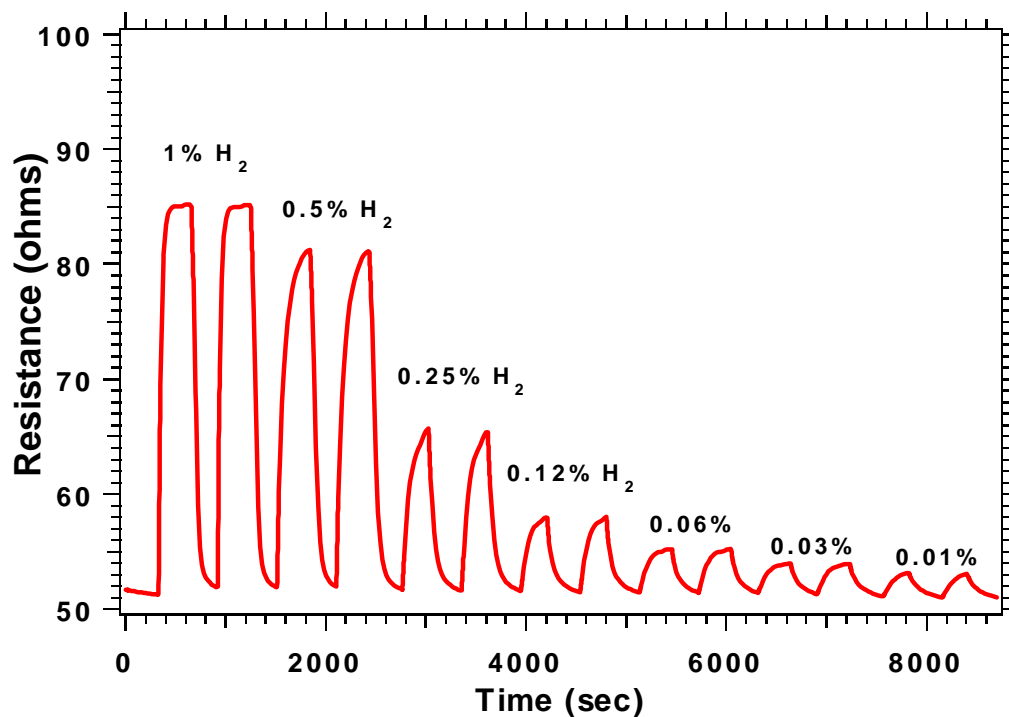


Figure 5. Resistive response of a microhotplate based H_2 gas sensor to concentrations of H_2 in air ranging from 1% to 0.01%.

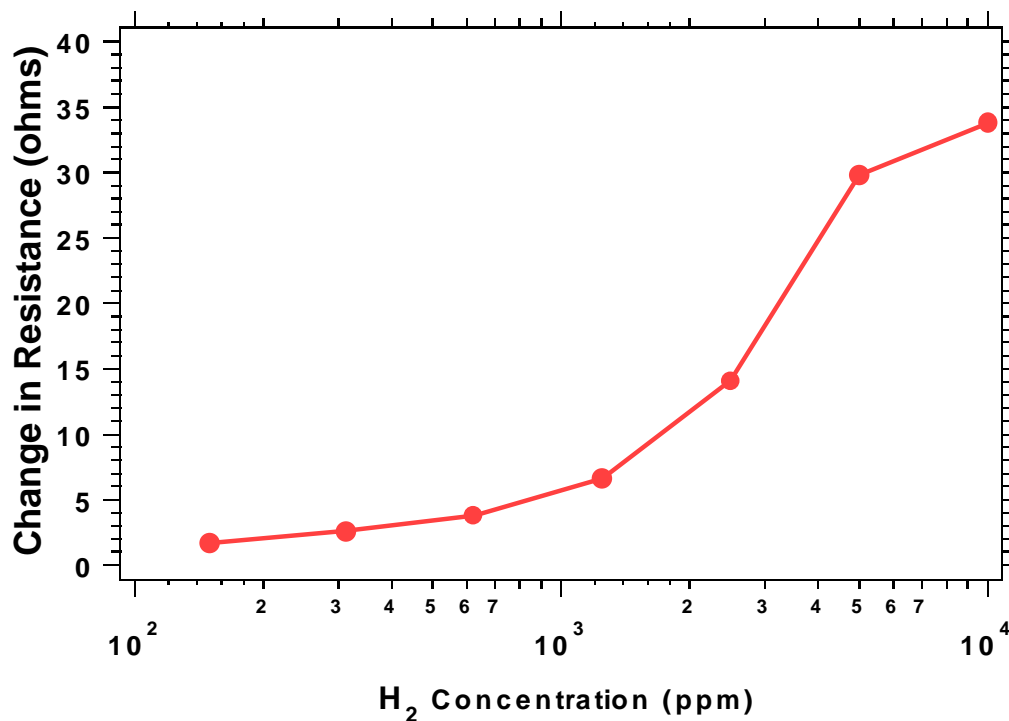


Figure 6. The resistive response from the previous figure, plotted as function of H_2 gas concentration.

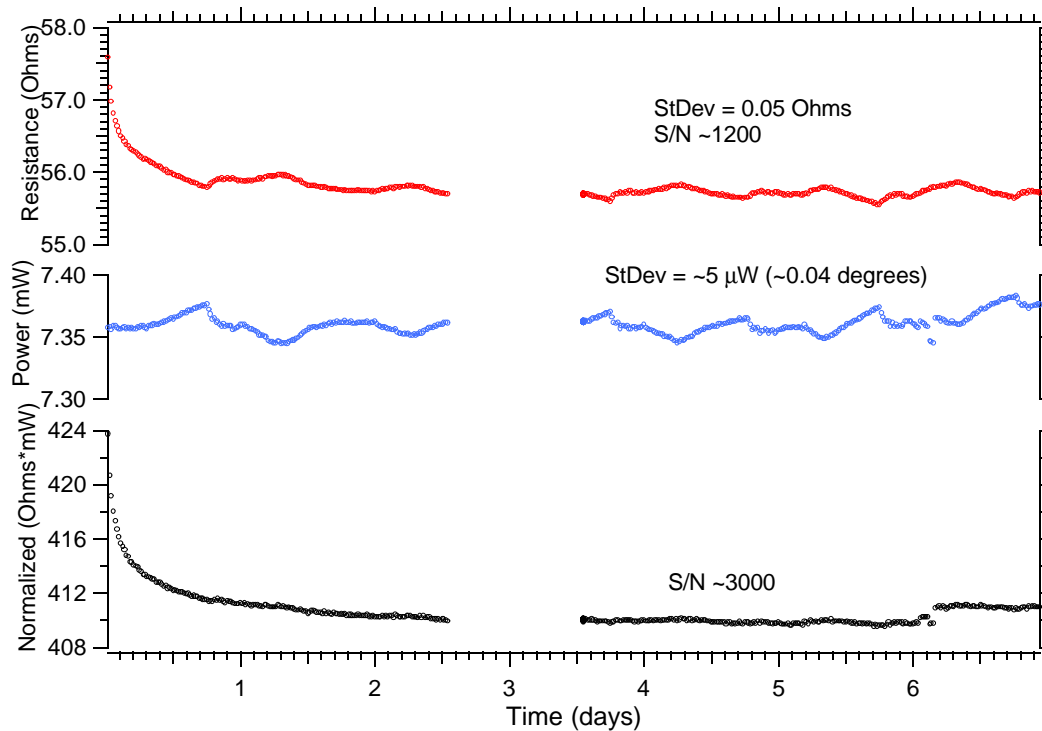


Figure 7. Stability results over a 7 day time frame. Top: H₂ sensor resistance in air. Middle: Measured poly silicon heater power. Bottom: Normalized sensor response (Resistance * Heater Power).

Economic Analysis

A significant advantage to the microhotplate based approach for H₂ gas sensing is that it is based on commercially available semiconductor processing technology. This technology is readily accessible through a number of integrated chip foundry facilities. The small size and simplicity of the microhotplate device can further leverage this advantage, and we therefore estimate that more than 1 million devices could be produced on a single lot of 25 six-inch wafers. Our analysis further indicates that at these quantities, the final device cost becomes dominated by the packaging costs.

Conclusions

In our work to date, we have successfully demonstrated a novel hydrogen gas sensing technology based on a MEMS device platform known as a microhotplate. These sensors have shown exceptional responsivity. Changes in resistance of >120% to 0.25 % H₂ concentrations have been measured, with response times <0.5 sec. These sensors have demonstrated a dynamic range of two orders of magnitude, detecting H₂ from >200ppm to > 1%. In the area of stability, we have demonstrated an un-corrected baseline signal to noise ratio of ~1200, and a temperature compensated signal to noise of ~3000. From a commercialization standpoint, our preliminary analysis indicates that this technology is

readily scalable to quantities > 1 million devices. These results are extremely encouraging and suggest that this technology has substantial potential for meeting the sensing requirements of a hydrogen based energy economy.

Future Work

Based on the successful demonstration of these devices, we plan to continue to focus our efforts on exploring the potential of these devices. We would like to continue to investigate the effect of sensor fabrication on sensor performance, as well as begin hydrogen response testing under different environment conditions, e.g. humid vs dry. We will also continue to investigate the long-term stability of these sensor materials under these different environments

Acknowledgements

The contributions of Frank Tamweber and Ed Hutchins of ATMI in the fabrication of the sensor devices and gas testing manifold respectively are gratefully acknowledged. Conversations with researchers at NIST, Steve Semancik and Dick Cavicchi, are also gratefully acknowledged. This work, performed at ATMI, was supported in part by the U.S. Department of Energy, under contract #DE-FC36-99GO10451. This support, however, does not constitute an endorsement by the DOE of the views expressed in this article.

References

- Baltes, H., O. Paul, et al. (1998). "Micromachined Thermally Based CMOS Microsensors." Proceedings of the IEEE **86**(8): 1660-1678.
- Bhandari, G. and T. H. Baum (1999). "Hydrogen sensor utilizing rare earth metal thin film detection element." US Patent 6,006,582
- Cavicchi, R. E., J. S. Suehle, et al. (1995). "Fast Temperature Programmed Sensing for Micro-Hotplate Gas Sensor." IEEE Electron Device Lett. **16**: 286-288.
- DOE (1995). Vision Statement, The Green Hydrogen Report; The 1995 Progress Report of the Secretary of Energy's Hydrogen Technical Advisory Panel., DOE.
- HRI/NREL (1998). The Sourcebook for Hydrogen Applications, Hydrogen Research Institute, National Renewable Energy Laboratory.
- Hunter, G. W. (1996). "PdTi Metal Alloy as a hydrogen or hydrocarbon sensitive metal." US Patent 5520753
- Suehle, J. S., R. E. Cavicchi, et al. (1993). "Tin Oxide Gas Sensor fabricated using CMOS Micro-hotplates and In Situ Processing." IEEE Electron Device Lett. **14**: 118-120.